

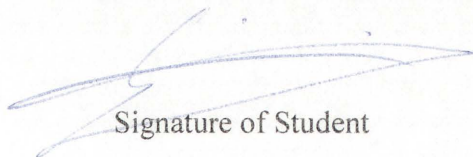
Tyre Profiling:
Development and Evolution of
Forensic Methodology

2009

CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.



Signature of Student

Acknowledgments

I would like to thank a number of people and organisations for their assistance and support in the completion of this research. Firstly and most importantly, I would like to thank my wife Tamar, who not only gave me the mental and emotional support I needed, but who was more than happy to accompany me to wherever my research took me. During this research we were also blessed with our son Luke, who has given me the mental breaks required when dealing with a project for so long. I would also like to thank the rest of my family for all their love and support over the past 6 years.

I would also like to thank my supervisor Brian Reedy who was always there when I needed him, and who gave me the much appreciated feedback and opinions that I needed. Thank you also to my initial supervisor Eric Du Pasquier, who got this research up and running all those years ago, and for arranging my visit to the IRCGN.

Many thanks must go to Jim Keegan whose help with the PyGCMS was invaluable considering the amount of time I spent on the instrument. I would not have been able to complete as much work as I did without Jim's help. Thanks also to Ron Shimmon for his help with the NMR, though in the end I didn't use any of it. Thanks to Katie McBean for her assistance in the examination of samples using the ESEM.

Thank you to Goodyear Castle Hill and Brookvale Tyres for the supply of tyres and sampling of tyres, to the NSW Police Driver Training unit for access to a road for the completion of the skid tests, and to the IRCGN for allowing me to stay on base and use their equipment for 6 weeks.

For their support over the years I would like to thank my fellow PhD students who are going through the same insanity as me, and who were always there not only to share ideas but who made the time spent doing this that much less painful. Thanks to my initial work colleagues who over the years gave me the time off I needed to get into the lab and get my work done, and thanks also to my current work colleagues who have given me a lot of support over the last two years.

Contents

Abstract	1
1 INTRODUCTION	3
1.1 Introduction	4
1.2 Aims of the Research	5
1.3 Tyres.....	7
1.3.1 Components of the Tyre Tread	9
1.3.2 Rubber.....	10
1.3.2.1 Natural Rubber	10
1.3.2.2 Synthetic Rubber.....	11
1.3.3 Extender Oils.....	13
1.3.4 Fillers	14
1.3.5 Vulcanisation.....	15
1.3.6 Accelerators.....	16
1.3.7 Activators	17
1.3.8 Processing Aids.....	17
1.3.8.1 Peptisers	17
1.3.8.2 Plasticisers and Softeners.....	18
1.3.9 Protective Agents	19
1.3.10 Manufacturing Process.....	20
1.3.10.1 Mastication	20
1.3.10.2 Mixing.....	21
1.3.10.3 Extruding and Calendering	21
1.4 Tyre Marks	23
1.5 Forensic Analysis of Tyres.....	26
1.6 Analysis of Polymers and Rubbers	29
1.7 References	34
2 METHOD DEVELOPMENT	39
2.1 Introduction	40
2.1.1 Aim.....	43

2.2	Materials and Methods	44
2.2.1	Instrument 1	44
2.2.1.1	Settings	45
2.2.1.2	Parameters	45
2.2.1.3	Samples	46
2.2.1.4	Data Analysis	46
2.2.2	Instrument 2	47
2.2.2.1	Settings	49
2.2.2.2	Parameters	49
2.2.2.3	Samples	50
2.2.2.4	Sample Preparation	50
2.3	Results and Discussion	51
2.3.1	Stage One – Selection of Pyrolysis Temperature	51
2.3.1.1	Polymer Content	51
2.3.1.2	Product Information	61
2.3.2	Stage Two – Selection of Chromatographic Program – Furnace Pyrolyser	64
2.3.3	Stage Three – Analysis using 30 m Column	70
2.3.4	Stage Four – Analysis using Pyroprobe	81
2.4	Conclusion	90
2.5	References	91
3	Analysis and Comparison of Tyres	94
3.1	Introduction	95
3.2	Materials and Methods	98
3.2.1	Samples	98
3.2.2	Pyrolysis Gas Chromatography/Mass Spectrometry	102
3.2.3	Environmental Scanning Electron Microscope (ESEM)	103
3.2.4	Data Analysis	103
3.3	Results and Discussion	105
3.3.1	Homogeneity of a Single Tyre	105
3.3.2	Homogeneity Over Time	112
3.3.3	Homogeneity of a Production Batch	120

3.3.4	Different Production Batches	122
3.3.5	Different Models	128
3.3.6	Different Sizes.....	129
3.4	Conclusion	132
3.5	References	134
4	Collection Techniques.....	136
4.1	Introduction	137
4.2	Materials and Methods.....	140
4.2.1	Collection Techniques.....	140
4.2.1.1	Hand Picking.....	140
4.2.1.2	Adhesive Tape.....	141
4.2.1.3	Fingerprint Lift.....	142
4.2.1.4	Clear Adhesive Tape	143
4.2.1.5	Swabbing.....	143
4.2.2	Pyrolysis Gas Chromatography/Mass Spectrometry	144
4.2.3	Environmental Scanning Electron Microscope (ESEM)	145
4.2.4	Brake Marks	146
4.2.5	Comparison of Techniques	147
4.3	Results and Discussion.....	147
4.3.1	Amount of Material.....	147
4.3.2	Size of Particles.....	151
4.3.3	Removal of Material from Collection Tool	153
4.3.4	Amount of Tyre Material Collected.....	156
4.3.5	Identification of Contaminants.....	162
4.4	Conclusion	168
4.5	References	169
5	CLASSIFICATION	170
5.1	Introduction	171
5.2	Materials & Methods.....	174
5.2.1	Samples	174
5.2.2	Pyrolysis Gas Chromatography/Mass Spectrometry	175

5.2.3	Tyre Residues.....	176
5.2.4	Data Analysis	177
5.3	Results and Discussion.....	178
5.3.1	Differences between the Tyre and the Residue.....	178
5.3.2	Target Compound Identification	187
5.3.3	Relative Polymer Content	189
5.3.4	Multivariate Analysis	194
5.4	Conclusion	201
5.5	References	203
6	Final Conclusions.....	204
6.1	Final Conclusions.....	205
A	Appendix A	208
A.1	Mass Spectra of Unidentified Peaks	208
B	Appendix B	242
B.1	Loadings of Nine Principal Components	242

List of Figures

Figure 1.1: Numerous components of a steel belted radial tyre.....	9
Figure 1.2: Monomer unit of <i>cis</i> -1,4-isoprene	11
Figure 1.3: Monomer unit of 1,4-styrene-butadiene	12
Figure 1.4: Monomer unit of 1,3-butadiene	12
Figure 1.5: Straight skid or braking marks on a section of road	23
Figure 1.6: Skid marks left by a turning vehicle. Three separate marks can be seen.	25
Figure 1.7: Rear wheels of a vehicle being intentionally spun without the vehicle moving.	25
Figure 2.1: Pyrolysis – Gas Chromatograph with Mass Spectrometer detector	44
Figure 2.2: Pyrolysis GC-FID with interface and pyroprobe.....	48
Figure 2.3: Tyre sample in quartz tube.	50
Figure 2.4: Bar graph showing the relative polymer content of each repeat analysis for the Bridgestone, Dunlop, and Firestone tyres when pyrolysed at 450 °C.....	51
Figure 2.5: Bar graph showing the relative polymer content of each repeat analysis for the Federal, Goodyear, and Hankook tyres when pyrolysed at 450 °C.	52
Figure 2.6: Bar graph showing the relative polymer content of each repeat analysis for the Nankang, Sime, and Toyo tyres when pyrolysed at 450 °C.....	52
Figure 2.7: Bar graph showing the relative polymer content of each repeat analysis for the Yokohama, Khumo, and Sumitomo tyres when pyrolysed at 450 °C.....	53
Figure 2.8: Bar graph showing the relative polymer content of each repeat analysis for the Bridgestone, Dunlop, and Firestone tyres when pyrolysed at 750 °C.....	55
Figure 2.9: Bar graph showing the relative polymer content of each repeat analysis for the Federal, Goodyear, and Hankook tyres when pyrolysed at 750 °C.	56
Figure 2.10: Bar graph showing the relative polymer content of each repeat analysis for the Nankang, Sime, and Toyo tyres when pyrolysed at 750 °C.....	56
Figure 2.11: Bar graph showing the relative polymer content of each repeat analysis for the Yokohama, Khumo, and Sumitomo tyres when pyrolysed at 450 °C.....	57

Figure 2.12: Bar graph of relative polymer content of all twelve tyres pyrolysed at 750 °C. For sample numbers refer to list on page 46.	60
Figure 2.13: Bar graph of relative polymer content of all twelve tyres pyrolysed at 450 °C. For sample numbers refer to list on page 46.	60
Figure 2.14a: Khumo Chromatogram at setting 1 – 450 °C, 8 °C/min and 60 m column. ..	64
Figure 2.14b: Khumo Chromatogram at setting 3 – 450 °C, 10 °C/min and 60 m column. ..	65
Figure 2.15: First three minutes of the chromatograms of the Sumitomo tyre analysed at Setting 1 and Setting 3. The chromatograms show the separation between the 1,3-butadiene and isoprene peaks.	65
Figure 2.16: Close up of styrene peak in chromatograms of the Firestone tyre analysed using Setting 1 and Setting 3.	67
Figure 2.17: Bar graph showing the relative polymer content of each repeat analysis for the Bridgestone, Dunlop, and Firestone tyres, when pyrolysed at 450 °C and analysed on the 30 m column.	70
Figure 2.18: Bar graph showing the relative polymer content of each repeat analysis for the Federal, Goodyear, and Hankook tyres, when pyrolysed at 450 °C and analysed on the 30 m column.	71
Figure 2.19: Bar graph showing the relative polymer content of each repeat analysis for the Nankang, Sime, and Toyo tyres, when pyrolysed at 450 °C and analysed on the 30 m column.	71
Figure 2.20: Bar graph showing the relative polymer content of each repeat analysis for the Yokohama, Khumo, and Sumitomo tyres, when pyrolysed at 450 °C and analysed on the 30 m column.	72
Figure 2.21: Chromatogram of Goodyear tyre pyrolysed at 450 °C and analysed on a 30 m column.	74
Figure 2.22: Chromatogram of Khumo tyre pyrolysed at 450 °C and analysed on a 30 m column.	74
Figure 2.23: Bar graph of average relative polymer content of all twelve tyres pyrolysed at 450 °C and analysed on the 30 m column.	75

Figure 2.24a: Chromatogram of Bridgestone tyre pyrolysed at 450 °C and analysed on 60 m column. Six peaks in the initial section are (from table 2.10): 1: 1,3 – butadiene, 2: isoprene, 4: 4 – vinylcyclohexene, 8: styrene, 12: methylstyrene, and 13: limonene.....	76
Figure 2.24b: Chromatogram of Bridgestone tyre pyrolysed at 450 °C and analysed on 30 m column. Six peaks in the initial section are (from table 2.10): 1: 1, 3 – butadiene, 2: isoprene, 4: 4 – vinylcyclohexene, 8: styrene, 12: methylstyrene, and 13: limonene.....	76
Figure 2.25: Mass spectrum of unidentified peak with retention time of 26.8 minutes on the 60m column, and 29.8 minutes on the 30 m column. This peak was present in all samples.	77
Figure 2.26: Relationship of unidentified peak 211/268 to stearic acid and hexadecanoic acid peaks on both 60 m column above and 30 m column below.....	78
Figure 2.27: Close up of 1,3-butadiene and isoprene peaks in chromatograms of the Dunlop tyre using 60 m column (above) and 30 m column (below).	79
Figure 2.28: Close up of 1,3-butadiene and isoprene peaks from chromatogram of the Federal tyre.....	79
Figure 2.29: Close up of 1,3-butadiene and isoprene peaks from chromatogram of Sumitomo tyre.....	80
Figure 2.30: Khumo tyre chromatogram pyrolysed at a static 750 °C for 15 s using Pyroprobe.	82
Figure 2.31: Bar graph of relative polymer content of seven tyres pyrolysed at a static 750 °C for 15s using the pyroprobe. Results are an average of three replicates. For sample numbers, see list on page 50.	83
Figure 2.32a: First repeat chromatogram of the Bridgestone tyre pyrolysed at a static 750 °C for 15s.	85
Figure 2.32b: Seventh repeat chromatogram of the Bridgestone tyre pyrolysed at a static 750 °C for 15s.	85
Figure 2.32c: Eighth repeat chromatogram of the Bridgestone tyre pyrolysed at a static 750 °C for 15s.	86
Figure 2.33: Chromatogram showing electrical artefacts.	87
Figure 2.34a: Chromatogram of the Hankook tyre analysed using pyroprobe at a static 750 °C for 15s	89

Figure 2.34b: Chromatogram of the Hankook tyre analysed using furnace pyrolyser at 450 °C.....	89
Figure 2.34c: Chromatogram of the Hankook tyre analysed using furnace pyrolyser at 750 °C.....	89
Figure 3.1: Six locations on the tyre from which samples were taken.	99
Figure 3.2: Relative Polymer Contents of Tyre 1	106
Figure 3.3: Relative Polymer Contents of Tyre 2	106
Figure 3.4: Relative Polymer Content of tyre 3	107
Figure 3.5: Relative polymer content of tyre 4	107
Figure 3.6: PCA scree plots of four Yokohama tyres before use.	109
Figure 3.7: Electron micrograph of tyre sample taken with GSE detector.	110
Figure 3.8: Electron micrograph of tyre sample taken with BSE detector.	111
Figure 3.9: Elemental analysis of thin threads on tyre sample. The threads are most likely silica.	111
Figure 3.10: Relative polymer content of tyre 1 at different distances.....	113
Figure 3.11: Relative polymer content of tyre 2 at different distances.....	113
Figure 3.12: Relative polymer content of tyre 3 at different distances.....	114
Figure 3.13: Relative polymer content of tyre 4 at different distances.....	114
Figure 3.14a: Chromatogram of sample of tyre 3 taken at 10,000 km	116
Figure 3.14b: Chromatogram of sample of tyre 3 taken at 30,000 km	116
Figure 3.15a: Chromatogram of sample of tyre 4 at 10,000 km	117
Figure 3.15b: Chromatogram of sample of tyre 4 at 20,000 km.....	117
Figure 3.15c: Chromatogram of sample of tyre 4 at 30,000 km	117
Figure 3.16: PCA scree plots of four Yokohama tyres over 20,000 km.....	118
Figure 3.17: Relative polymer content of ten Yokohama S760 tyres all from the same production batch.....	120
Figure 3.18: Relative polymer content of ten Toyo Proxes H4 tyres from four different production batches.	122
Figure 3.19a: Chromatogram of Toyo tyre number 1, batch number 1303 with tall, narrow styrene peak.....	124

Figure 3.19b: Chromatogram of Toyo tyre number 3, batch number 1303 with short, broad styrene peak.....	124
Figure 3.20: Scree plot of Toyo production batches	125
Figure 3.21 Score plot of PC1 vs PC2 of Toyo production batch	125
Figure 3.22: Scree plot of Toyo production batches without ‘outlier’	126
Figure 3.23 Score plot of PC1 vs PC2 of Toyo production batch without ‘outlier’.	126
Figure 3.24: Relative polymer content of four different Yokohama model tyres all of the same size.	128
Figure 3.25: Relative polymer content of six Yokohama S306 tyres of different sizes. ...	129
Figure 3.26: Tread patterns of four different model Yokohama tyres12	130
Figure 4.1: Metal tweezers used for picking.....	141
Figure 4.2: 4” x 4” Fingerprint lift placed on braking mark on bitumen road.....	142
Figure 4.3: Material collected from aggregate road (left) and bitumen road (right) using 4” x 4” fingerprint lift.	148
Figure 4.4: Material collected from aggregate road (left) and bitumen road (right) using clear adhesive tape (4cm wide).	149
Figure 4.5: Different amounts of tyre material collected using five swabs on a tyre smear on a concrete road surface.....	150
Figure 4.6a: Tyre particle picked from aggregate road surface viewed with scanning electron microscope and GSE detector.	152
Figure 4.6b: Tyre particle collected with fingerprint lift from bitumen road viewed with scanning electron microscope and BSE detector.	152
Figure 4.6c: Tyre particle collected with clear adhesive tape from bitumen road viewed with scanning electron microscope and BSE detector.	153
Figure 4.7: Tyre particles embedded in adhesive after treatment with solvent. The solvent removed the adhesive from the backing, but did not separate the adhesive from the particles.	155
Figure 4.8: Chromatogram of tyre particle collected by picking from skid mark on aggregate road. Peaks are – 1: 1, 3-butadiene; 2: Isoprene; 3: Vinylcyclohexene; 4: Styrene; 5: Limonene; 6: 4-phenylcyclohexene; 7: 1, 3-diphenylpropane; 8: Diisooctyl phthalate.	156

Figure 4.9: Chromatogram of tyre particle collected from aggregate road with a fingerprint lift. Adhesive peaks are 1: 2-Ethylhexene, (E)-4-Octene, and (Z)-4-Octene; 2: Cyclooctane; 3: 2-Ethyl-4-methylpentanol; 4: 2-Propenoic acid, 6-methylheptyl ester, and Ethylhexanol; 5: Octyl methacrylate. 157

Figure 4.10: Chromatogram of tyre particle collected from aggregate road using clear adhesive tape. The second half of the chromatogram shows small additive peaks 1: Butanedioic acid, methyl-, bis(1-methylpropyl) ester, 2: .alpha.-Methylcaprolactam. 157

Figure 4.11: Chromatogram of tyre particle picked from bitumen road..... 158

Figure 4.12: Chromatogram of second tyre particle picked from bitumen road..... 158

Figure 4.13: Chromatogram of Yokohama particle picked from bitumen road. 159

Figure 4.14: Chromatogram of tyre particle picked from bitumen road, after being washed with a benzene: ethanol wash..... 159

Figure 4.15: Chromatogram of blank cotton swab..... 160

Figure 4.16: Chromatogram of blackened cotton swab (acetone solvent). Peak A: Butyl methacrylate. None of the peaks present are similar to those found in tyre samples. 160

Figure 4.17: Chromatogram of blackened swab pyrolysed at 750°C. Three peaks were identified as potentially coming from the tyre: 1. Styrene, 2. Indene, and 3. Naphthalene. 161

Figure 4.18: Chromatogram of bitumen..... 163

Figure 4.19: Chromatogram of fingerprint lift adhesive. Peak assignments are shown in table 4.7. 163

Figure 4.20: Chromatogram of adhesive from clear tape. Peak assignments are shown on table 4.7. 164

Figure 4.21: Chromatogram of Sime tyre residue collected using fingerprint lift. Twelve of the fourteen peaks from the fingerprint lift adhesive are identified. (Peak assignments are in Table 4.7) 164

Figure 4.22: Chromatograms of firestone tyre particles collected using fingerprint lift showing differences due to adhesive contamination. The first chromatogram has a limonene peak at a retention time of 12.7 minutes, where the second chromatogram has a 2-Ethyl-4-methylpentanol peak due to the adhesive at the same retention time. Other peaks associated with fingerprint lift are labelled according to table 4.7..... 167

Figure 5.1: Short section of skid mark on concrete road with gravel aggregate.....	176
Figure 5.2: Residue collected from skid mark.	181
Figure 5.3a: Mass Spectra at 19.05 minutes in the chromatogram of the Bridgestone sample.	182
Figure 5.3b: Mass Spectra at 19.05 minutes in the chromatogram of the Dunlop sample.	182
Figure 5.3c: Mass Spectra at 19.05 minutes in the chromatogram of the Dunlop residue.	183
Figure 5.4a: Mass Spectra at 22.10 Minutes in the chromatogram of the Bridgestone sample.	183
Figure 5.4b: Mass Spectra at 22.10 Minutes in the chromatogram of the Dunlop sample.	183
Figure 5.4c: Mass Spectra at 22.10 Minutes in the chromatogram of the Dunlop residue.	183
Figure 5.5a: Position of peak in both Goodyear sample and residue.	184
Figure 5.5b: Different spectra of peaks with the same retention time. This shows a change from the tyre sample to the residue.	185
Figure 5.6: Butadiene and Isoprene peaks in the chromatogram of the Hankook tyre sample.	189
Figure 5.7: Butadiene and isoprene peaks in the chromatogram of the Nankang tyre sample.	189
Figure 5.8: Butadiene and isoprene peaks in the chromatogram of the Federal tyre sample.	190
Figure 5.9: Scree plot of tyre samples.....	194
Figure 5.10: Scree plot of residues.....	195
Figure 5.11: Scree plot of tyre samples and residues.....	195
Figure 5.12: Score plot of PC1 v PC2 of the tyre samples	197
Figure 5.13: Score plot of PC1 v PC2 of residues.	197
Figure A.1: Mass Spectra of Peak No. 3, Unidentified 1.....	208
Figure A.2: Mass Spectra of Peak No. 23, Unidentified 2.....	208
Figure A.3: Mass Spectra of Peak No. 24, Unidentified 3.....	208
Figure A.4: Mass Spectra of Peak No. 25, Unidentified 4.....	209
Figure A.5: Mass Spectra of Peak No. 26, Unidentified 5.....	209
Figure A.6: Mass Spectra of Peak No. 27, Unidentified 6.....	209
Figure A.7: Mass Spectra of Peak No. 30, Unidentified 7.....	210

Figure A.8: Mass Spectra of Peak No. 31, Unidentified 8.....	210
Figure A.9: Mass Spectra of Peak No. 32, Unidentified 9.....	210
Figure A.10: Mass Spectra of Peak No. 33, Unidentified 10.....	211
Figure A.11: Mass Spectra of Peak No. 35, Unidentified 11.....	211
Figure A.12: Mass Spectra of Peak No. 36, Unidentified 12.....	211
Figure A.13: Mass Spectra of Peak No. 37, Unidentified 13.....	212
Figure A.14: Mass Spectra of Peak No. 39, Unidentified 14.....	212
Figure A.15: Mass Spectra of Peak No. 40, Unidentified 15.....	212
Figure A.16: Mass Spectra of Peak No. 41, Unidentified 16.....	213
Figure A.17: Mass Spectra of Peak No. 43, Unidentified 17.....	213
Figure A.18: Mass Spectra of Peak No. 44, Unidentified 18.....	213
Figure A.19: Mass Spectra of Peak No. 45, Unidentified 19.....	214
Figure A.20: Mass Spectra of Peak No. 46, Unidentified 20.....	214
Figure A.21: Mass Spectra of Peak No. 47, Unidentified 21.....	214
Figure A.22: Mass Spectra of Peak No. 48, Unidentified 22.....	215
Figure A.23: Mass Spectra of Peak No. 49, Unidentified 23.....	215
Figure A.24: Mass Spectra of Peak No. 51, Unidentified 24.....	215
Figure A.25: Mass Spectra of Peak No. 53, Unidentified 25.....	216
Figure A.26: Mass Spectra of Peak No. 57, Unidentified 26.....	216
Figure A.27: Mass Spectra of Peak No. 59, Unidentified 27.....	216
Figure A.28: Mass Spectra of Peak No. 60, Unidentified 28.....	217
Figure A.29: Mass Spectra of Peak No. 60, Unidentified 29.....	217
Figure A.30: Mass Spectra of Peak No. 65, Unidentified 30.....	217
Figure A.31: Mass Spectra of Peak No. 67, Unidentified 31.....	218
Figure A.32: Mass Spectra of Peak No. 68, Unidentified 32.....	218
Figure A.33: Mass Spectra of Peak No. 72, Unidentified 33.....	218
Figure A.34: Mass Spectra of Peak No. 73, Unidentified 34.....	219
Figure A.35: Mass Spectra of Peak No. 76, Unidentified 35.....	219
Figure A.36: Mass Spectra of Peak No. 77, Unidentified 36.....	219
Figure A.37: Mass Spectra of Peak No. 78, Unidentified 37.....	220
Figure A.38: Mass Spectra of Peak No. 81, Unidentified 38.....	220

Figure A.39: Mass Spectra of Peak No. 82, Unidentified 39..... 220

Figure A.40: Mass Spectra of Peak No. 83, Unidentified 40..... 221

Figure A.41: Mass Spectra of Peak No. 84, Unidentified 41..... 221

Figure A.42: Mass Spectra of Peak No. 85, Unidentified 42..... 221

Figure A.43: Mass Spectra of Peak No. 86, Unidentified 43..... 222

Figure A.44: Mass Spectra of Peak No. 87, Unidentified 44..... 222

Figure A.45: Mass Spectra of Peak No. 88, Unidentified 45..... 222

Figure A.46: Mass Spectra of Peak No. 91, Unidentified 46..... 223

Figure A.47: Mass Spectra of Peak No. 92, Unidentified 47..... 223

Figure A.48: Mass Spectra of Peak No. 93, Unidentified 48..... 223

Figure A.49: Mass Spectra of Peak No. 95, Unidentified 49..... 224

Figure A.50: Mass Spectra of Peak No. 96, Unidentified 50..... 224

Figure A.51: Mass Spectra of Peak No. 98, Unidentified 51..... 224

Figure A.52: Mass Spectra of Peak No. 100, Unidentified 52..... 225

Figure A.53: Mass Spectra of Peak No. 101, Unidentified 53..... 225

Figure A.54: Mass Spectra of Peak No. 102, Unidentified 54..... 225

Figure A.55: Mass Spectra of Peak No. 103, Unidentified 55..... 226

Figure A.56: Mass Spectra of Peak No. 104, Unidentified 56..... 226

Figure A.57: Mass Spectra of Peak No. 105, Unidentified 57..... 226

Figure A.58: Mass Spectra of Peak No. 106, Unidentified 58..... 227

Figure A.59: Mass Spectra of Peak No. 107, Unidentified 59..... 227

Figure A.60: Mass Spectra of Peak No. 108, Unidentified 60..... 227

Figure A.61: Mass Spectra of Peak No. 109, Unidentified 61..... 228

Figure A.62: Mass Spectra of Peak No. 110, Unidentified 62..... 228

Figure A.63: Mass Spectra of Peak No. 111, Unidentified 63..... 228

Figure A.64: Mass Spectra of Peak No. 112, Unidentified 64..... 229

Figure A.65: Mass Spectra of Peak No. 113, Unidentified 65..... 229

Figure A.66: Mass Spectra of Peak No. 114, Unidentified 66..... 229

Figure A.67: Mass Spectra of Peak No. 115, Unidentified 67..... 230

Figure A.68: Mass Spectra of Peak No. 116, Unidentified 68..... 230

Figure A.69: Mass Spectra of Peak No. 117, Unidentified 69..... 230

Figure A.70: Mass Spectra of Peak No. 118, Unidentified 70.....	231
Figure A.71: Mass Spectra of Peak No. 119, Unidentified 71.....	231
Figure A.72: Mass Spectra of Peak No. 121, Unidentified 72.....	231
Figure A.73: Mass Spectra of Peak No. 122, Unidentified 73.....	232
Figure A.74: Mass Spectra of Peak No. 124, Unidentified 74.....	232
Figure A.75: Mass Spectra of Peak No. 127, Unidentified 75.....	232
Figure A.76: Mass Spectra of Peak No. 128, Unidentified 76.....	233
Figure A.77: Mass Spectra of Peak No. 129, Unidentified 77.....	233
Figure A.78: Mass Spectra of Peak No. 130, Unidentified 78.....	233
Figure A.79: Mass Spectra of Peak No. 131, Unidentified 79.....	234
Figure A.80: Mass Spectra of Peak No. 132, Unidentified 80.....	234
Figure A.81: Mass Spectra of Peak No. 133, Unidentified 81.....	234
Figure A.82: Mass Spectra of Peak No. 134, Unidentified 82.....	235
Figure A.83: Mass Spectra of Peak No. 135, Unidentified 83.....	235
Figure A.84: Mass Spectra of Peak No. 137, Unidentified 84.....	235
Figure A.85: Mass Spectra of Peak No. 139, Unidentified 85.....	236
Figure A.86: Mass Spectra of Peak No. 140, Unidentified 86.....	236
Figure A.87: Mass Spectra of Peak No. 142, Unidentified 87.....	236
Figure A.88: Mass Spectra of Peak No. 143, Unidentified 88.....	237
Figure A.89: Mass Spectra of Peak No. 144, Unidentified 89.....	237
Figure A.90: Mass Spectra of Peak No. 145, Unidentified 90.....	237
Figure A.91: Mass Spectra of Peak No. 147, Unidentified 91.....	238
Figure A.92: Mass Spectra of Peak No. 148, Unidentified 92.....	238
Figure A.93: Mass Spectra of Peak No. 151, Unidentified 93.....	238
Figure A.94: Mass Spectra of Peak No. 154, Unidentified 94.....	239
Figure A.95: Mass Spectra of Peak No. 155, Unidentified 95.....	239
Figure A.96: Mass Spectra of Peak No. 156, Unidentified 96.....	239
Figure A.97: Mass Spectra of Peak No. 157, Unidentified 97.....	240
Figure A.98: Mass Spectra of Peak No. 158, Unidentified 98.....	240
Figure A.99: Mass Spectra of Peak No. 160, Unidentified 99.....	240
Figure A.100: Mass Spectra of Peak No. 161, Unidentified 100.....	241

Figure A.101: Mass Spectra of Peak No. 162, Unidentified 101..... 241

List of Tables

Table 2.1: Different pyrolysis settings used by authors	41
Table 2.2: Different chromatographic settings used by authors	42
Table 2.3: Settings used for pyrolysis and chromatograph oven	45
Table 2.4: GC parameters	45
Table 2.5: Equations used to calculate relative polymer content.....	47
Table 2.6: Pyrolysis conditions examined using Pyroprobe.	49
Table 2.7: GC parameters used with Pyroprobe	49
Table 2.8: Relative polymer content (%) and variance values for all repeats of all 12 samples pyrolysed at 450 °C	54
Table 2.9: Relative polymer content (%) and variance values for all repeats of all 12 samples pyrolysed at 750 °C	58
Table 2.10: Compounds tentatively identified from mass spectrum data from all tyres pyrolysed at 450 °C, and their potential source within the sample. The list is a composite one, and not all of these compounds are common to all the tyres.	62
Table 2.11: Compounds tentatively identified from mass spectrum data from all tyres pyrolysed at 750 °C, and their potential source within the sample. The list is a composite one, and not all of these compounds are common to all the tyres.	63
Table 2.12: Resolution between butadiene peak and isoprene peak calculated for each sample pyrolysed at 450 °C at each chromatographic temperature program.....	66
Table 2.13: Relative polymer contents (%) for all twelve tyre samples	69
Table 2.14: Variance values calculated for each of the three polymers at both PyGCMS settings	69
Table 2.15: Relative polymer content (%) and variance values for all repeats of all twelve samples pyrolysed at 450 °C and analysed on the 30 m column	73
Table 2.16: Pyrolysis conditions employed on the pyroprobe and the findings	81
Table 2.17: Relative polymer content (%) and variance values for all seven tyres pyrolysed at a static 750 °C for 15s on pyroprobe. Results are the average of three replicates.	82

Table 2.18: Relative polymer content and variance values for all repeats of seven samples pyrolysed at a static 750 °C for 15s using the pyroprobe.....	84
Table 3.1: Tyres used to investigate the homogeneity of a single tyre and of a tyre over time.....	98
Table 3.2: Tyres used to investigate the homogeneity of a single production batch	100
Table 3.3: Tyres used to investigate the homogeneity of different production batches	100
Table 3.4: Tyres used to compare different models of the same size from the same manufacturer.	101
Table 3.5: Tyres used to compare different sizes of the same model and same manufacturer.	101
Table 3.6: GC Parameters	102
Table 3.7: Equations used to calculate relative polymer content.....	103
Table 3.8: Relative Polymer Content of six locations on the four different tyres listed in table 3.1.	105
Table 3.9: Relative polymer contents of the four tyres at three different distances.....	112
Table 3.10: Relative polymer contents of ten Yokohama tyres from the same production batch.	120
Table 3.11: Relative polymer contents of ten Toyo tyres from four different production batches.....	122
Table 3.12: Relative polymer content of four different Yokohama model tyres of the same size.....	128
Table 3.13: Relative polymer contents of six Yokohama S306 tyres of different sizes. ...	129
Table 4.1: Solvents tested on adhesive	141
Table 4.2: GC Parameters	144
Table 4.3: Tyres used to create braking marks	146
Table 4.4: Results of different collection media in collecting sufficient material for analysis.	148
Table 4.5: Results for solvents tested on adhesives from clear tape and fingerprint lift. ..	154
Table 4.6: Identification of the contaminated and non-contaminated repeat analyses.	162
Table 4.7: Components of fingerprint lift adhesive and clear adhesive tape.	165
Table 5.1: Parameters used for Py-GC/MS program	175

Table 5.2: Identified and unidentified compounds observed in all twelve tyre samples...	179
Table 5.2 cont'd: Identified and unidentified compounds observed in all twelve tyre samples.....	180
Table 5.3: The 43 consistent compounds used for the TCI, PCA and LDA.....	186
Table 5.4: Presence and absence of eight peaks within the twelve tyre samples.....	187
Table 5.5: Presence and absence of eight peaks within the twelve residues.....	188
Table 5.6: The ranges of RPC for each of the twelve tyres.	190
Table 5.7: Six classification groups based on RPC ranges	191
Table 5.8: RPC values for each of the residues.	192
Table 5.9: Classification results of all residues.....	193
Table 5.10: Eigenvalues of the first nine principal components for the tyre samples, residues, and tyre samples and residues combined.	196
Table 5.11: LDA classification results using 43 original variables.	198
Table 5.12: LDA classification results using nine principal components.....	199
Table B.1: Loadings of nine PCs of tyre samples alone	242
Table B.2: Loadings of nine PCs of tyre residues alone.....	243
Table B.3: Loadings of nine PCs of tyre samples and residues.....	244

Abstract

The chemical analysis of tyres is not a routine part of forensic investigation. The use of tyres as evidence has been limited to comparison of the tread pattern. However, the tread pattern is not the only evidence that may be left behind by a tyre. When a tyre skids across a hard road surface such as bitumen or concrete, residue from the tyre may be left behind.

It was the aim of this research to develop a method for the analysis of tyres and their residues, understand the amount of chemical variation in tyres, identify suitable methods for the collection of tyre residues from different road surfaces, and to classify tyre samples and identify the source of tyre residues.

A suitable method for analysis was successfully developed using pyrolysis-gas chromatography/mass spectrometry. It was found that pyrolysis was best completed at 450 °C using a furnace type pyrolyser.

Chemical variation was investigated in a single tyre, in tyres over time, in production batches, and between different models and sizes of tyres from the same manufacturer. Small variations were found within a single tyre and in tyres over time. Greater variation was observed in both the same and different production batches, and between different model tyres and different size tyres.

Three different collection techniques were investigated – picking, adhesive tape, and swabbing. Picking was found to be the most suitable technique to use on a concrete road with gravel aggregate, while a fingerprint lift was found to be the most suitable technique on a bitumen road surface. Swabbing was found to be an unsuitable technique.

Six replicate analyses were used to catalogue changes in the chemical composition between the tyre and the residue. Numerous changes were observed such that only a limited number of signals from the chromatogram could be used for identification purposes. Three different techniques were used for classification and identification – relative polymer content (RPC), target compound identification (TCI), and linear discriminant analysis (LDA). LDA was found to be the most successful technique, correctly classifying 31 of 36 tyre residues.

PyGCMS allows for simple analysis of tyre samples and residues without pre-treatment. A tyre sample was found to have 5-10% variation in the relative polymer content, regardless of when during the life of the tyre the sample was taken. Variation was found between tyres from the same manufacturer. Both similarities and differences were found between tyres from the same production batch and different production batches, suggesting that homogeneity in a single production batch not guaranteed and that manufacturers will also change the composition of a tyre between different production batches. The collection of tyre residues (like the collection of any forensic evidence) may or may not be successful depending specifically on the type of road surface. Collection of tyre residues from a concrete road with gravel aggregate was successfully achieved through picking. Collection of tyre residues from a bitumen road was successfully achieved; however adhesive contamination from both the fingerprint lift and clear adhesive tape interfered with the PyGCMS analysis. Tyre residues were successfully correlated to the source tyre, but the process of collecting sample information from numerous replicate analyses of both the tyre sample and residue for data analysis was a time-consuming one.